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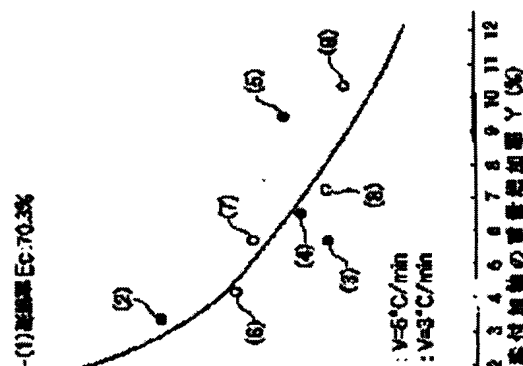
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(54) METHOD OF MANUFACTURING ACTIVATED CARBON FOR ELECTRIC DOUBLE-LAYER CAPACITOR, AND POLARIZABLE ELECTRODE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide activated carbon for an electrode, where the amount of expansion upon charging can be reduced, when a polarizable electrode for an electric double-layer capacitor is constituted.

SOLUTION: When activated carbon for an electrode are manufactured, this method employs the steps of subjecting a material for activated carbon, which is an



aggregate of individual bodies, to oxygenation treatment to obtain an oxygen adduct in which oxygen is dispersed inside each entire individual body, subjecting the oxygen adduct to carbonization treatment to obtain a carbonized material and subjecting the carbonized material to activation treatment, to obtain activated carbon.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the activated carbon for electrodes of an electric double layer capacitor, and a polarizable electrode.

[0002]

[Description of the Prior Art] Conventionally, as this kind of the manufacture approach, the increment in electrostatic capacity is aimed at and the method of performing carbonization processing and alkali activation processing using KOH one by one is learned, using the raw material for graphitizing carbon as a raw material for activated carbon.

[0003]

[Problem(s) to be Solved by the Invention] However, since the amount of expansion at the time of charge of the polarizable electrode is large when a polarizable electrode is constituted using the activated carbon for electrodes by the conventional method, For example, although it is necessary to provide a means to raise case reinforcement in order to prepare the space corresponding to said amount of expansion in a case in the electric double layer capacitor of a laminating mold or a winding mold or to receive the expansion force In the case of the former, the fault of the fall of the electrostatic capacity per unit volume is invited, and, on the other hand, in the case of the latter, faults, such as a rise of case cost and case weight increase, are invited.

[0004]

[Means for Solving the Problem] This invention aims at offering said manufacture approach that the activated carbon for electrodes which can reduce the amount of expansion at the time of the charge can be obtained, when a polarizable electrode is constituted.

[0005] Oxygen attached processing gives the raw material for activated carbon which is the set object of an individual according to this invention in order to attain said purpose, and the manufacture approach of the activated carbon of an electric double layer capacitor for electrodes using the process which obtains the oxygen addition product which made the whole interior of these individuals distribute oxygen, the process which perform carbonization processing to the oxygen addition product, and obtain carbonization material, and the process which perform activation processing to the carbonization material, and obtain activated carbon is offered.

[0006] When the above oxygen attached processing was performed and a polarizable electrode is constituted using the activated carbon pass subsequent carbonization processing and activation processing, the amount of expansion at the time of charge of the polarizable electrode can be reduced.

[0007] Moreover, this invention aims at offering the polarizable electrode for electric double layer capacitors with the small amount of expansion at the time of charge.

[0008] In order to attain said purpose, according to this invention, it has activated carbon obtained by performing oxygen attached processing before carbonization processing, and the polarizable electrode of an electric double layer capacitor whose expansion coefficient E_c at the time of charge termination is $E_c \leq 50\%$ is offered.

[0009] The desired end can be attained if constituted as mentioned above.

[0010]

[Embodiment of the Invention] In drawing 1, the carbon button mold electric double layer capacitor 1 has the spacer 5 inserted between the polarizable electrodes 3 and 4 of a pair held in a case 2 and its case 2, and them, and the electrolytic solution with which it filled up in the case 2. A case 2 consists of a cover plate 8 made from aluminum which closes the vessel body 7 made from aluminum which has opening 6, and its opening 6, and the seal of between the periphery section of the cover plate 8 and the inner circumference section of a vessel body 7 is carried out by the sealant 9. Each polarizable electrodes 3 and 4 consist of mixture of activated carbon, an electric conduction filler, and a binder.

[0011] In manufacture of the activated carbon for electrodes, oxygen attached processing is given to the raw material for activated carbon which is the set object of an individual, and the process which obtains the oxygen addition product which made the whole interior of these individuals distribute oxygen, the process which performs carbonization processing to the oxygen addition product, and obtains carbonization material, and the process which performs activation processing to the carbonization material, and obtains activated carbon are used. Grinding processing is performed to the carbonization material obtained by carbonization processing if needed.

[0012] When the above oxygen attached processing is performed, the whole interior of two or more individuals was made to distribute oxygen and polarizable electrodes 3 and 4 are constituted using the activated carbon pass subsequent carbonization processing and activation processing, the amount of expansion at the time of charge of these polarizable electrodes 3 and 4 can be reduced.

[0013] As a raw material for activated carbon, powder, a fiber set object (the set object of the fibrous object by spinning is included), etc. which consist of raw materials for graphitizing carbon, such as a petroleum pitch, a mesophase pitch, a coal pitch, a meso carbon micro bead, polyimide, and PAN, are used. Therefore, the individual in powder is one particle and the individual in a fiber set object is either one fiber or a fibrous object. In order to diffuse oxygen, the magnitude of these particles, fiber, and a fibrous object comes out [particle] the average diameter of 20 micrometers or less about the mean particle diameter of 20 micrometers or less, fiber, and a fibrous object, and a certain thing is desirable. After oxygen attached processing is a predetermined programming rate, and heats the raw material for activated carbon to predetermined temperature in air or reaches predetermined temperature, it is carried out to the temperature by the approach of carrying out predetermined time maintenance.

[0014] In this case, if weight of the raw material for activated carbon is set to W and the weight of W+ oxygen of an oxygen addition product, i.e., the amount, is set to X, the weight rate of increase Y by oxygen attached processing will be expressed as $Y = \{(X - W) / W\} \times 100(\%)$, and that weight rate of increase Y will be set up to $2\% \leq Y \leq 20\%$. $Y < 2\%$ of the amount depressor effect of expansion of a polarizable electrode is [the weight rate of increase Y] insufficient, on the other hand, at $Y > 20\%$, during carbonization processing of degree process, carbon burns and the yield of carbonization material decreases. The weight rate of increase Y is $Y \geq 3.5\%$ preferably.

[0015] Said programming rate V in oxygen attached processing in order to store the above weight rate of increase Y in said range is $1 \text{ degree C} / \text{min} \leq V \leq 20 \text{ degrees C} / \text{min}$. Moreover, whenever [stoving temperature], T1 is set as $250 \text{ degree-C} \leq T1 \leq 350 \text{ degree C}$, and (holding-time h) t1 is set up further in $10\text{-}3\text{-hour} \leq t1 \leq 10 \text{ hours}$, respectively.

[0016] Moreover, P2 O5, a quinone, a hydroquinone, etc. may use the derivative which makes these a subject that oxygen attached processing should be promoted.

[0017] Carbonization processing is performed based on the well-known conditions adopted in this kind of the manufacture approach. Namely, among an inert gas ambient atmosphere, whenever [stoving temperature], $T2 \text{ is set as } 600 \text{ degree-C} \leq T2 \leq 1000 \text{ degree C}$, and heating time t2 is set up in $10 \text{ to } 3 \text{ hour} \leq t2 \leq 10 \text{ hours}$, respectively.

[0018] The alkali activation processing using KOH as activation processing is applied, and that alkali activation processing is performed based on the well-known conditions adopted in this kind of the manufacture approach. Namely, among an inert gas ambient atmosphere, whenever [stoving temperature], $T3 \text{ is set as } 500 \text{ degree-C} \leq T3 \leq 1000 \text{ degree C}$, and heating time t3 is set up in $10 \text{ to } 3$

hour $\leq t \leq 10$ hours, respectively.

[0019] Hereafter, an example is explained.

[0020] A. The set object which consists of a fibrous object with an average diameter of 14 micrometers was obtained by performing spinning using the manufacture 1. oxygen (attached-processing a) mesophase pitch of fibrous activated carbon. (b) Examples 1-9 of an oxygen addition product were acquired by performing oxygen attached processing which differs in conditions using the set object. (c) It asked for the weight rate of increase Y about Examples 1-9.

[0021] Table 1 shows the conditions of oxygen attached processing and the weight rate of increase Y about Examples 1-9.

[0022]

[Table 1]

酸素付 加物	酸素付加処理条件			重量増加率 Y (%)
	昇温速度 V (°C/min)	加熱温度 T 1 (°C)	保持時間 t 1 (h)	
例 1	2 8	2 8 0	—	1. 0
例 2	5	2 8 0	—	3. 5
例 3	5	3 0 0	—	5. 9
例 4	5	3 2 0	—	6. 7
例 5	5	3 2 0	0. 5	9. 7
例 6	3	2 8 0	—	4. 3
例 7	3	3 0 0	—	5. 9
例 8	3	3 2 0	—	7. 4
例 9	3	3 2 0	2. 0	1 0. 6

[0023] In Table 1, when there is no publication of the holding time and whenever [furnace temperature] becomes whenever [stoving temperature], it means having taken out the oxygen addition product from the processing furnace immediately.

[0024] 2. 700 degrees C and carbonization processing of 1 hour were performed to Examples 1-9 of a carbonization processing oxygen addition product among the nitrogen air current, subsequently grinding processing was performed, and Examples 1-9 of the graphitizing carbon fiber corresponding to these examples 1-9 were acquired.

[0025] The true density of Examples 1-9 is as in Table 2. The specific gravity converting method for having used the butanol estimated true density.

[0026]

[Table 2]

炭素繊維	真密度 (g/cc)
例 1	1.55
例 2	1.57
例 3	1.56
例 4	1.58
例 5	1.57
例 6	1.69
例 7	1.59
例 8	1.61
例 9	1.72

[0027] Next, about Examples 1, 6, and 9, with the electron ray step scan of TEM-EDX, when the oxygen density in the diameter part of each carbon fiber was investigated, the result of drawing 2 -4 was obtained.

[0028] As for drawing 2, addition oxygen exists about Example 1 only at the periphery section of a carbon fiber, and addition oxygen does not exist inside it. each carbon fiber from which a this addition oxygen's existence condition constitutes Example 1 -- abbreviation -- it was the same. This example 1 is equivalent to the conventional non-deliqesce processing object so that clearly from the oxygen attached-processing conditions of Table 1.

[0029] Drawing 3 is made into Example 6, and Seki of drawing 4 is made to Example 9, respectively, and it turns out that addition oxygen is distributing inside [whole] a carbon fiber in both the examples 6 and 9. Although there are few amounts of addition oxygen of a core and its near compared with it of the periphery section in Example 6 of drawing 3 since there are few amounts of addition oxygen than Example 9 of drawing 4, in the case of Example 9, there are many amounts of addition oxygen, and addition oxygen is distributing it to abbreviation homogeneity inside a carbon fiber in connection with it. each carbon fiber from which the addition oxygen distribution condition of drawing 4 constitutes Example 9 about each carbon fiber from which the addition oxygen distribution condition of drawing 3 constitutes Example 6 -- respectively -- abbreviation -- it was the same. each carbon fiber in which an addition oxygen distribution condition constitutes each example from these things also in each remaining examples -- abbreviation -- it can be said that it is the same.

[0030] 3. KOH was used for Examples 1-9 of an alkali activation processing carbon fiber, alkali activation processing which consists of 400 degrees C, primary processing of 1 hour and 800 degrees C, and secondary treatment of 5 hours into a nitrogen air current was performed, and Examples 1-9 of the fibrous activated carbon with an average diameter of 14 micrometers corresponding to Examples 1-9 were acquired.

[0031] B. The electrode sheet with a thickness of 185 micrometers was manufactured by carrying out weighing capacity of Example 1, carbon black (electric conduction filler), and PTFE (binder) of manufacture fibrous activated carbon of a carbon button mold electric double layer capacitor so that it may become the weight ratio of 85.6:9.4:5, kneading the weighing capacity object subsequently, and rolling out after that using a kneading object. The polarizable electrodes 3 and 4 with a diameter of 20mm of two sheets were cut down from the electrode sheet, and the carbon button mold electric double layer capacitor 1 of drawing 1 was manufactured using the polarizable electrodes 3 and 4 of these two sheets, the diameter of 25mm, the spacer 5 made from a glass fiber with a thickness of 0.35mm, the electrolytic solution, etc. As the electrolytic solution, the propylene carbonate solution of the triethyl

methylammonium tetrafluoro borate [(C₂H₅)₃CH₃NBF₄] of 2.0M was used.

[0032] Thus, let the carbon button mold electric double layer capacitor using Example 1 of activated carbon be a sample 1. Moreover, the samples 2-9 of a carbon button mold electric double layer capacitor were manufactured by said same approach using Example 1 and Examples 2-9 of the activated carbon which has the same fiber length.

[0033] C. About the electrostatic-capacity consistency of activated carbon, and the electric resistance value aforementioned sample 1 of a polarizable electrode, the following charge and discharge tests were performed and, subsequently the electrostatic-capacity consistency (F/g and F/cc) and electric resistance value of Example 1 of activated carbon were calculated by the energy converting method. In the charge and discharge test, the approach of performing charge for 90 minutes and discharge for 90 minutes in 2.7V was adopted. The same charge and discharge test was performed also about samples 2-9, and it asked for the electrostatic-capacity consistency of Examples 2-9 of activated carbon etc.

[0034] D. As shown in calculation drawing 5 of the expansion coefficient E_c of a polarizable electrode, said same polarizable electrode 3 of two sheets using Example 1 of activated carbon and the layered product 10 which made 40mm long, 40mm wide, and the spacer 5 made of a nonwoven fabric with a thickness of 0.24mm intervene among four were made into the sample 1, and this was installed on the inner base of the cistern 11 made from aluminum. In the cistern 11, said same electrolytic solution 12 was poured in, subsequently to the top face of the upper polarizable electrode 3, the copper vertical section 14 lower-limit side of the pressurization object 13 was laid, and the vertical section 14 and a cistern 11 were further connected to the charge-and-discharge circuit 17 through path cords 15 and 16. In the condition of having set the load of the pressurization object 13 over the biparite polarity electrodes 3 and 4 as 3kg Charge and discharge called discharge are repeated using the charge-and-discharge circuit 17 in 5mA of constant current, and 5mA of constant current which ranks second to charge and it in constant-voltage 2.7V for 2 hours. A deed and the amount of the maximum expansion in the thickness direction of the biparite polarity electrodes 3 and 4 at the time of charge, i.e., the maximum thickness of a layered product 10, were measured using a laser displacement gage as an amount of displacement of the pressurization object 13. And thickness before charge of a layered product 10 was set to T_a , and on the other hand, when the volume at the time of charge termination of a layered product 10 was set to T_b , the expansion coefficient E_c of a polarizable electrode was computed as $E_c = \{(T_b - T_a) / T_a\} \times 100(\%)$.

[0035] The samples 2-9 with the polarizable electrodes [measurement / same] 3 and 4 using Examples 2-9 of activated carbon of a layered product 10 were followed.

[0036] E. The consideration table 3 shows the electrode consistency about samples (the carbon button mold electric double layer capacitor 1 and a layered product 10 are included) 1-9, the electrostatic-capacity consistency (F/g) of the activated carbon per unit weight, the electrostatic-capacity consistency per unit volume (F/cc), and the expansion coefficient E_c of a polarizable electrode. In Table 3, the weight rate of increase Y in the oxygen addition product of Table 1 was carried for convenience.

[0037]

[Table 3]

試料	電極密度 (g/cc)	静電容量密度		分極性電極の 膨脹率 E c (%)	酸素付加物の 重量増加率 Y (%)
		(F/g)	(F/cc)		
1	0.88	35.36	31.19	70.3	1.0
2	0.80	38.17	30.38	47.0	3.5
3	0.79	36.70	29.00	38.0	5.9
4	0.80	37.56	30.00	39.5	6.7
5	0.80	38.23	30.47	40.3	9.7
6	0.84	35.88	30.00	43.0	4.3
7	0.87	35.83	31.10	42.0	5.9
8	0.85	36.06	30.62	38.0	7.4
9	0.88	36.30	31.18	37.0	10.6

[0038] Drawing 6 graph-izes relation of the weight rate of increase Y of an oxygen addition product and the expansion coefficient Ec of a polarizable electrode about samples 1-9 based on Table 3. (1) - (9) corresponds to samples 1-9 among drawing, respectively.

[0039] If the weight rate of increase Y of an oxygen addition product is made to increase so that clearly from drawing 6, the expansion coefficient Ec of polarizable electrodes 3 and 4 will decrease. In this case, at Y= 1.0%, the expansion coefficient Ec of polarizable electrodes 3 and 4 exceeds [the weight rate of increase Y of an oxygen addition product] 50% like a sample 1.

[0040]

[Effect of the Invention] When a polarizable electrode is constituted by adopting the above means according to invention of claim 1 and three publications, the manufacture approach of the activated carbon for electrodes of an electric double layer capacitor which can obtain the activated carbon which can reduce the amount of expansion at the time of the charge can be offered.

[0041] When a polarizable electrode is constituted by adopting the above means according to invention of claims 2 and 4 and five publications, the manufacture approach of the activated carbon for electrodes of an electric double layer capacitor which can obtain the activated carbon which can reduce much more certainly the amount of expansion at the time of the charge can be offered.

[0042] According to invention according to claim 6, the polarizable electrode for electric double layer capacitors with the small amount of expansion at the time of charge can be offered.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the activated carbon of the electric double layer capacitor characterized by to give oxygen attached processing to the raw material for activated carbon which is the set object of an individual, and to use the process which obtains the oxygen addition product which made the whole interior of these individuals distribute oxygen, the process which performs carbonization processing to the oxygen addition product, and obtains carbonization material, and the process which performs activation processing to the carbonization material, and obtains activated carbon for electrodes.

[Claim 2] When weight of said raw material for activated carbon is set to W and weight of said oxygen addition product is set to X, the weight rate of increase Y by said oxygen attached processing is the manufacture approach of the activated carbon for electrodes of an electric double layer capacitor according to claim 1 which is $2\% \leq Y \leq 20\%$.

[Claim 3] The manufacture approach of the activated carbon of the electric double layer capacitor characterized by to give oxygen attached processing to the raw material for graphitizing carbon which is the set object of an individual, and to use the process which obtains the oxygen addition product which made the whole interior of these individuals distribute oxygen, the process which perform carbonization processing to the oxygen addition product, and obtain carbonization material, and the process which perform alkali activation processing to the carbonization material, and obtain activated carbon for electrodes.

[Claim 4] When weight of said raw material for graphitizing carbon is set to W and weight of said oxygen addition product is set to X, the weight rate of increase Y by said oxygen attached processing is the manufacture approach of the activated carbon for electrodes of an electric double layer capacitor according to claim 3 which is $Y \geq 3.5\%$.

[Claim 5] Said individual in said raw material for graphitizing carbon is the manufacture approach of the activated carbon for electrodes of an electric double layer capacitor according to claim 3 or 4 of being either fiber or a fibrous object and performing said grinding processing after carbonization processing.

[Claim 6] The polarizable electrode of the electric double layer capacitor which has activated carbon obtained by performing oxygen attached processing before carbonization processing, and is characterized by the expansion coefficient Ec at the time of charge termination being $Ec \leq 50\%$.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the important section fracture front view of a carbon button mold electric double layer capacitor.

[Drawing 2] It is the graph which shows the oxygen density in an example of a carbon fiber.

[Drawing 3] It is the graph which shows the oxygen density in the other examples of a carbon fiber.

[Drawing 4] It is the graph which shows the oxygen density in other examples of a carbon fiber further.

[Drawing 5] It is the schematic diagram of the expansion coefficient measuring device of a polarizable electrode.

[Drawing 6] It is the graph which shows the relation between the weight rate of increase Y of an oxygen addition product, and the expansion coefficient E_c of a polarizable electrode.

[Description of Notations]

1 Carbon button mold electric double layer capacitor

3 4 Polarizable electrode

[Translation done.]

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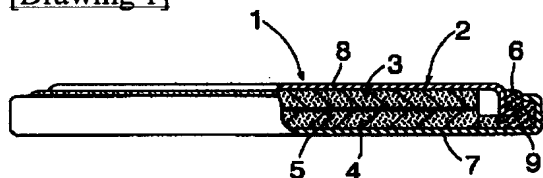
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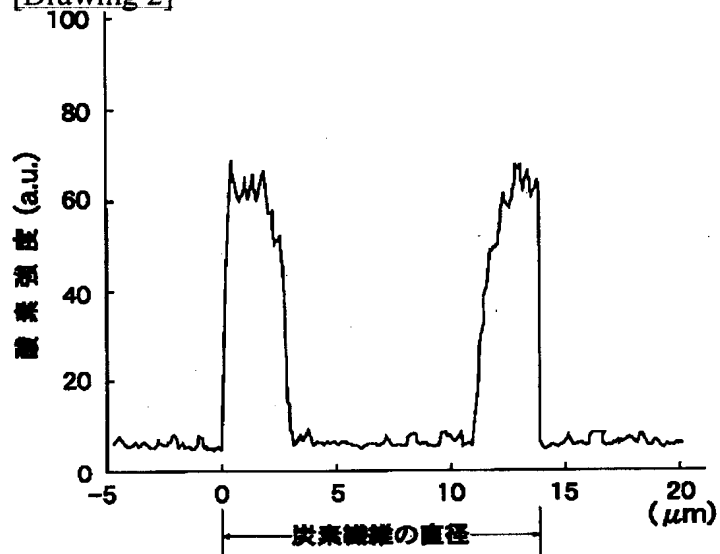
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DRAWINGS

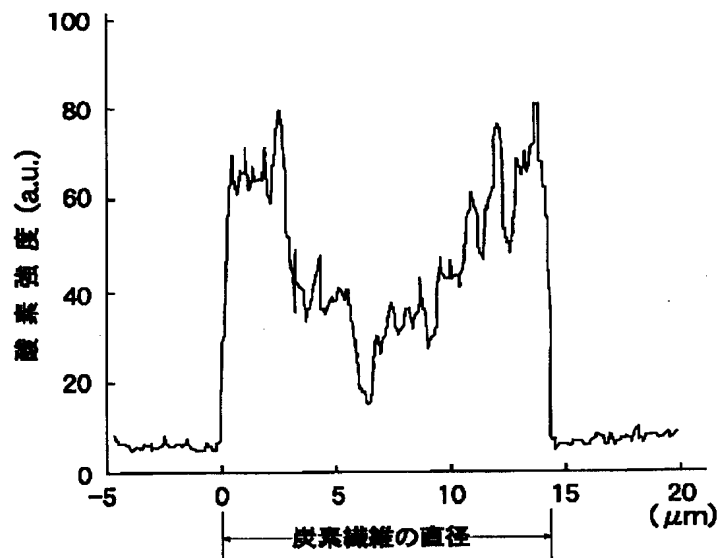
[Drawing 1]



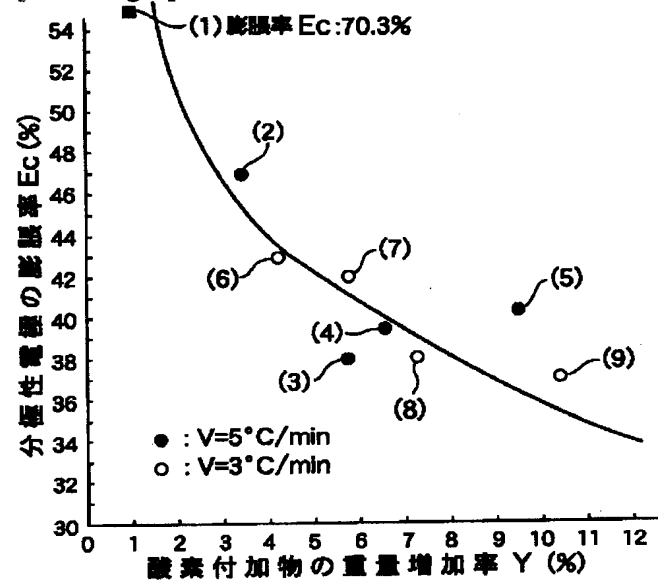
[Drawing 2]



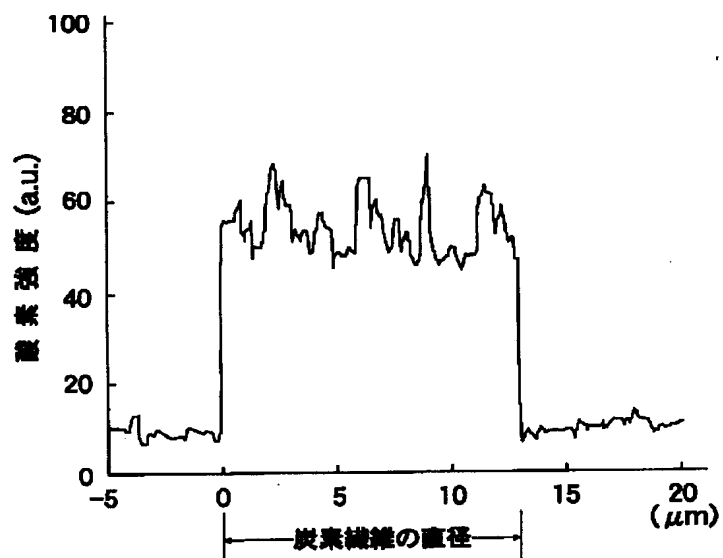
[Drawing 3]



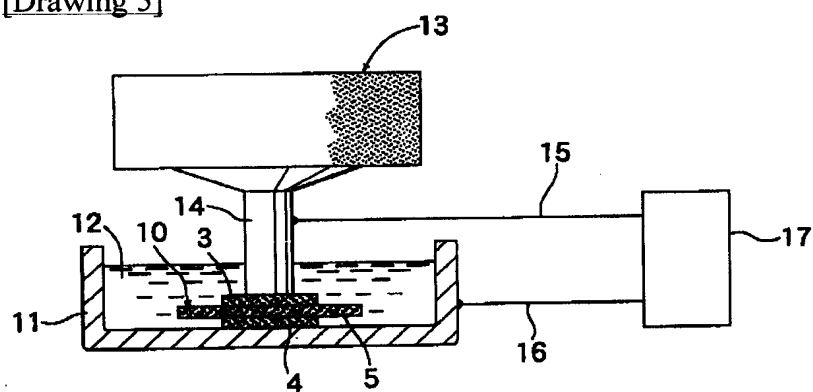
[Drawing 6]



[Drawing 4]



[Drawing 5]



[Translation done.]

METHOD OF MANUFACTURING ACTIVATED CARBON FOR ELECTRIC DOUBLE-LAYER CAPACITOR, AND POLARIZABLE ELECTRODE

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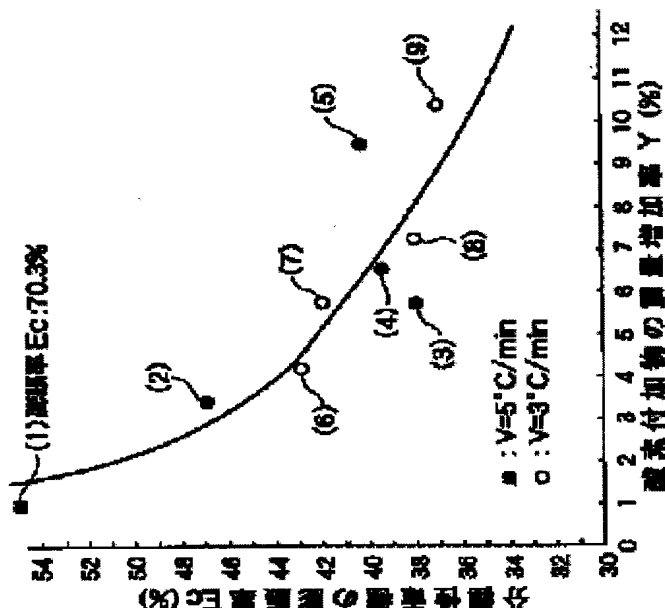
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Abstract of JP2002134369

PROBLEM TO BE SOLVED: To provide activated carbon for an electrode, where the amount of expansion upon charging can be reduced, when a polarizable electrode for an electric double-layer capacitor is constituted.

SOLUTION: When activated carbon for an electrode are manufactured, this method employs the steps of subjecting a material for activated carbon, which is an aggregate of individual bodies, to oxygenation treatment to obtain an oxygen adduct in which oxygen is dispersed inside each entire individual body, subjecting the oxygen adduct to carbonization treatment to obtain a carbonized material and subjecting the carbonized material to activation treatment, to obtain activated carbon.



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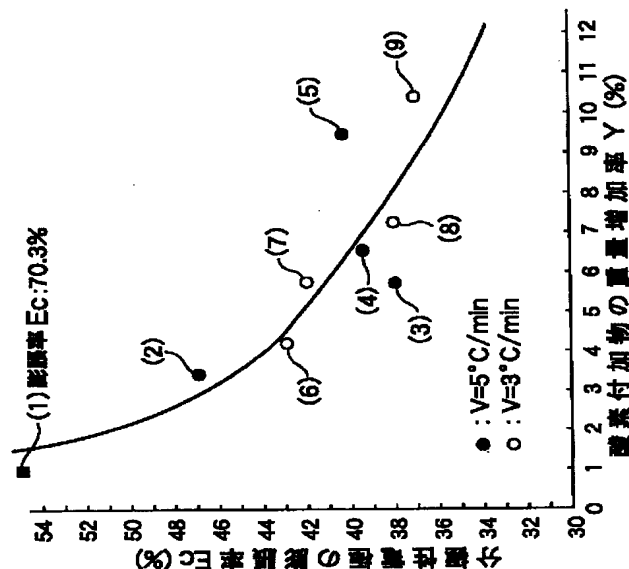
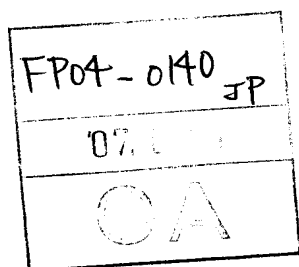
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(54) 【発明の名称】 電気二重層コンデンサの電極用活性炭の製造方法および分極性電極

(57) 【要約】

【課題】 電気二重層コンデンサの分極性電極を構成した場合、その充電時における膨脹量を低減することが可能な電極用活性炭を得る。

【解決手段】 電極用活性炭を製造するに当り、個体の集合物である活性炭用原料に酸素付加処理を施して、それら個体の内部全体に酸素を分散させた酸素付加物を得る工程と、その酸素付加物に炭化処理を施して炭化材を得る工程と、その炭化材に賦活処理を施して活性炭を得る工程とを用いる。



【特許請求の範囲】

【請求項 1】 個体の集合体である活性炭用原料に酸素付加処理を施して、それら個体の内部全体に酸素を分散させた酸素付加物を得る工程と、その酸素付加物に炭化処理を施して炭化材を得る工程と、その炭化材に賦活処理を施して活性炭を得る工程とを用いることを特徴とする電気二重層コンデンサの電極用活性炭の製造方法。

【請求項 2】 前記活性炭用原料の重量を W とし、また前記酸素付加物の重量を X とすると、前記酸素付加処理による重量増加率 Y は $2\% \leq Y \leq 20\%$ である、請求項 1 記載の電気二重層コンデンサの電極用活性炭の製造方法。

【請求項 3】 個体の集合体である易黒鉛化性炭素用原料に酸素付加処理を施して、それら個体の内部全体に酸素を分散させた酸素付加物を得る工程と、その酸素付加物に炭化処理を施して炭化材を得る工程と、その炭化材にアルカリ賦活処理を施して活性炭を得る工程とを用いることを特徴とする電気二重層コンデンサの電極用活性炭の製造方法。

【請求項 4】 前記易黒鉛化性炭素用原料の重量を W とし、また前記酸素付加物の重量を X とすると、前記酸素付加処理による重量増加率 Y は $Y \geq 3.5\%$ である、請求項 3 記載の電気二重層コンデンサの電極用活性炭の製造方法。

【請求項 5】 前記易黒鉛化性炭素用原料における前記個体は繊維および繊維状物の一方であり、前記炭化処理後粉碎処理を行う、請求項 3 または 4 記載の電気二重層コンデンサの電極用活性炭の製造方法。

【請求項 6】 炭化処理の前に酸素付加処理を行って得られた活性炭を有し、充電終了時における膨脹率 E_c が $E_c \leq 50\%$ であることを特徴とする電気二重層コンデンサの分極性電極。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は電気二重層コンデンサの電極用活性炭の製造方法および分極性電極に関する。

【0002】

【従来の技術】 従来、この種の製造方法としては、静電容量の増加を狙い、活性炭用原料として易黒鉛化性炭素用原料を用い、炭化処理および KOH を用いたアルカリ賦活処理を順次行う、といった方法が知られている。

【0003】

【発明が解決しようとする課題】 しかしながら、従来法による電極用活性炭を用いて分極性電極を構成すると、その分極性電極の、充電時における膨脹量が大きいため、例えば、積層型や巻回型の電気二重層コンデンサにおいては、ケース内に前記膨脹量に見合う空間を設けるか、またはその膨脹力を受けるためにケース強度を高める、といった手段を講じることが必要となるが、前者の

場合は単位容積当りの静電容量の低下、といった不具合を招来し、一方、後者の場合はケースコストの上昇、ケース重量の増加等の不具合を招来する。

【0004】

【課題を解決するための手段】 本発明は、分極性電極を構成した場合、その充電時における膨脹量を低減することが可能な電極用活性炭を得ることができる前記製造方法を提供することを目的とする。

【0005】 前記目的を達成するため本発明によれば、個体の集合体である活性炭用原料に酸素付加処理を施して、それら個体の内部全体に酸素を分散させた酸素付加物を得る工程と、その酸素付加物に炭化処理を施して炭化材を得る工程と、その炭化材に賦活処理を施して活性炭を得る工程とを用いる、電気二重層コンデンサの電極用活性炭の製造方法が提供される。

【0006】 前記のような酸素付加処理を行うと、その後の炭化処理および賦活処理を経て得られた活性炭を用いて分極性電極を構成した場合、その分極性電極の、充電時における膨脹量を低減することができる。

【0007】 また本発明は充電時における膨脹量の小さな電気二重層コンデンサ用分極性電極を提供することを目的とする。

【0008】 前記目的を達成するため本発明によれば、炭化処理の前に酸素付加処理を行って得られた活性炭を有し、充電終了時における膨脹率 E_c が $E_c \leq 50\%$ である、電気二重層コンデンサの分極性電極が提供される。

【0009】 前記のように構成すると所期の目的を達成することができる。

【0010】

【発明の実施の形態】 図 1 において、ボタン型電気二重層コンデンサ 1 は、ケース 2 と、そのケース 2 内に收容された一対の分極性電極 3、4 およびそれらの間に挟まれたスペーサ 5 と、ケース 2 内に充填された電解液とを有する。ケース 2 は開口部 6 を有する A1 製器体 7 およびその開口部 6 を閉鎖する A1 製蓋板 8 よりなり、その蓋板 8 の外周部および器体 7 の内周部間はシール材 9 によりシールされている。各分極性電極 3、4 は活性炭、導電フィラおよび結着剤の混合物よりなる。

【0011】 電極用活性炭の製造に当っては、個体の集合体である活性炭用原料に酸素付加処理を施して、それら個体の内部全体に酸素を分散させた酸素付加物を得る工程と、その酸素付加物に炭化処理を施して炭化材を得る工程と、その炭化材に賦活処理を施して活性炭を得る工程とが用いられる。必要に応じて、炭化処理により得られた炭化材に粉碎処理が施される。

【0012】 前記のような酸素付加処理を行って複数の個体の内部全体に酸素を分散させると、その後の炭化処理および賦活処理を経て得られた活性炭を用いて分極性電極 3、4 を構成した場合、それら分極性電極 3、4 の

充電時における膨脹量を低減することができる。

【0013】活性炭用原料としては、石油ピッチ、メソフェーズピッチ、石炭ピッチ、メソカーボンマイクロビーズ、ポリイミド、PAN等の易黒鉛化性炭素用原料よりなる粉末、繊維集合物（紡糸による繊維状物の集合物を含む）等が用いられる。したがって、粉末における個体は1つの粒子であり、繊維集合物における個体は1本の繊維および繊維状物の一方である。酸素を拡散させるために、これら粒子、繊維および繊維状物の大きさは、粒子については平均粒径 $20\mu\text{m}$ 以下、また繊維および繊維状物については平均直径 $20\mu\text{m}$ 以下、であることが望ましい。酸素付加処理は、活性炭用原料を空気中にて、所定の昇温速度で、所定の温度まで加熱するか、または所定の温度に達した後、その温度に所定時間保持する、といった方法で行われる。

【0014】この場合、活性炭用原料の重量をWとし、また酸素付加物の重量、つまりW+酸素量をXとすると、酸素付加処理による重量増加率Yは、 $Y = \{(X - W) / W\} \times 100 (\%)$ と表わされ、その重量増加率Yは、 $2\% \leq Y \leq 20\%$ に設定される。重量増加率Yが $Y < 2\%$ では分極性電極の膨脹量抑制効果が不十分であり、一方、 $Y > 20\%$ では次工程の炭化処理中に炭素が燃焼して炭化材の収量が減少する。重量増加率Yは、好ましくは $Y \geq 3.5\%$ である。

【0015】前記のような重量増加率Yを前記範囲に収めるべく、酸素付加処理における前記昇温速度Vは $1^\circ\text{C}/\text{min} \leq V \leq 20^\circ\text{C}/\text{min}$ に、また加熱温度T1は $250^\circ\text{C} \leq T1 \leq 350^\circ\text{C}$ に、さらに保持時間(h) t1は*

* 10^{-3} 時間 $\leq t1 \leq 10$ 時間にそれぞれ設定される。

【0016】また酸素付加処理を促進すべく、 P_2O_5 、キノン、ヒドロキノン等、またはこれらを主体とする誘導体等を用いてもよい。

【0017】炭化処理は、この種の製造方法において採用されている公知の条件に基づいて行われる。即ち、不活性ガス雰囲気中、加熱温度T2は $600^\circ\text{C} \leq T2 \leq 1000^\circ\text{C}$ に、また加熱時間t2は 10^{-3} 時間 $\leq t2 \leq 10$ 時間にそれぞれ設定される。

【0018】賦活処理としてはKOHを用いたアルカリ賦活処理が適用され、そのアルカリ賦活処理は、この種の製造方法において採用されている公知の条件に基づいて行われる。即ち、不活性ガス雰囲気中、加熱温度T3は $500^\circ\text{C} \leq T3 \leq 1000^\circ\text{C}$ に、また加熱時間t3は 10^{-3} 時間 $\leq t3 \leq 10$ 時間にそれぞれ設定される。

【0019】以下、具体例について説明する。

【0020】A. 繊維状活性炭の製造

1. 酸素付加処理

(a) メソフェーズピッチを用い、紡糸を行うことによって、平均直径 $14\mu\text{m}$ の繊維状物よりなる集合物を得た。(b) その集合物を用い、条件を異にする酸素付加処理を行うことによって、酸素付加物の例1～9を得た。(c) 例1～9について重量増加率Yを求めた。

【0021】表1は、例1～9に関する酸素付加処理の条件および重量増加率Yを示す。

【0022】

【表1】

酸素付加物	酸素付加処理条件			重量増加率Y (%)
	昇温速度V ($^\circ\text{C}/\text{min}$)	加熱温度T1 ($^\circ\text{C}$)	保持時間t1 (h)	
例1	28	280	—	1.0
例2	5	280	—	3.5
例3	5	300	—	5.9
例4	5	320	—	6.7
例5	5	320	0.5	9.7
例6	3	280	—	4.3
例7	3	300	—	5.9
例8	3	320	—	7.4
例9	3	320	2.0	10.6

【0023】表1において、保持時間の記載が無い場合は、炉内温度が加熱温度に達したとき、酸素付加物を処理炉から直ちに取出したことを意味する。

【0024】2. 炭化処理

酸素付加物の例1～9に、窒素気流中、 700°C 、1時

間の炭化処理を施し、次いで粉碎処理を行って、それら例1～9に対応する易黒鉛化性炭素繊維の例1～9を得た。

【0025】例1～9の真密度は表2の通りである。真密度については、ブタノールを用いた比重換算法により

評価を行った。

【0026】

【表2】

炭素繊維	真密度 (g/cc)
例1	1.55
例2	1.57
例3	1.56
例4	1.58
例5	1.57
例6	1.69
例7	1.59
例8	1.61
例9	1.72

【0027】次に、例1、6、9について、TEM-EDXの電子線ステップスキャンにより、各炭素繊維の直径部分における酸素濃度を調べたところ、図2～4の結果を得た。

【0028】図2は例1に関するもので、炭素繊維の外周部にのみ付加酸素が存在し、それよりも内側には付加酸素は存在しない。この付加酸素の存在状態は例1を構成する各炭素繊維について略同じであった。この例1は、表1の酸素付加処理条件から明らかなように、従来の不融化処理物に相当する。

【0029】図3は例6に、また図4は例9にそれぞれ関するもので、両例6、9においては炭素繊維の内部全体に付加酸素が分散していることが判る。図3の例6においては付加酸素量が図4の例9よりも少ないため、中心部およびその近傍の付加酸素量が外周部のそれに比べて少ないが、例9の場合は付加酸素量が多く、それに伴い付加酸素が炭素繊維の内部に略均一に分散している。図3の付加酸素分散状態は例6を構成する各炭素繊維について、また図4の付加酸素分散状態は例9を構成する各炭素繊維についてそれぞれ略同じであった。これらのことから、残りの各例においても付加酸素分散状態は各例を構成する各炭素繊維について略同じである、と言える。

【0030】3. アルカリ賦活処理

炭素繊維の例1～9に、KOHを用い、窒素気流中において、400℃、1時間の1次処理および800℃、5時間の2次処理よりなるアルカリ賦活処理を施して、例1～9に対応する、平均直径14μmの繊維状活性炭の例1～9を得た。

【0031】B. ボタン型電気二重層コンデンサの製作

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繊維状活性炭の例1、カーボンブラック（導電フィラ）およびPTFE（結着剤）を85：6：9：4：5の重量比となるように秤量し、次いでその秤量物を混練し、その後、混練物を用いて圧延を行うことによって、厚さ185μmの電極シートを製作した。電極シートから直径20mmの2枚の分極性電極3、4を切出し、これら2枚の分極性電極3、4、直径25mm、厚さ0.35mmのガラス繊維製スペーサ5、電解液等を用いて図1のボタン型電気二重層コンデンサ1を製作した。電解液としては、2.0Mのトリエチルメチルアンモニウム・テトラフルオロボレート $[(C_2H_5)_3CH_3NBF_4]$ のプロピレンカーボネート溶液を用いた。

【0032】このように活性炭の例1を用いたボタン型電気二重層コンデンサを試料1とする。また例1と同様の繊維長を有する活性炭の例2～9を用い、前記同様の方法で、ボタン型電気二重層コンデンサの試料2～9を製作した。

【0033】C. 活性炭の静電容量密度および分極性電極の電気抵抗値

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前記試料1について、次のような充放電試験を行い、次いでエネルギー換算法にて活性炭の例1の静電容量密度(F/g, F/cc)および電気抵抗値を求めた。充放電試験では、90分間の充電および90分間の放電を、2.7Vにて行う、といった方法を採用した。同様の充放電試験を試料2～9についても行って、活性炭の例2～9の静電容量密度等を求めた。

【0034】D. 分極性電極の膨脹率Ecの算出

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図5に示すように、活性炭の例1を用いた、前記同様の2枚の分極性電極3、4間に縦40mm、横40mm、厚さ0.24mmの不織布製スペーサ5を介在させた積層体10を試料1とし、これをA1製液槽11の内底面上に設置した。液槽11内に、前記同様の電解液12を注入し、次いで加圧体13の銅製鉛直部14下端面を上側の分極性電極3の上面に載置し、さらに鉛直部14および液槽11を接続線15、16を介して充放電回路17に接続した。両分極性電極3、4に対する加圧体13の荷重を3kgに設定した状態において、充放電回路17を用い、定電流5mA、定電圧2.7Vにて2時間充電、それに次ぎ定電流5mAにて放電、といった充放電を繰返して行い、充電時における両分極性電極3、4の厚さ方向における最大膨脹量、つまり積層体10の最大厚さを加圧体13の変位量としてレーザ変位計を用いて測定した。そして、積層体10の充電前の厚さをTaとし、一方、積層体10の充電終了時の体積をTbとしたとき、分極性電極の膨脹率Ecを $Ec = \{(Tb - Ta) / Ta\} \times 100 (\%)$ として算出した。

【0035】同様の測定を、活性炭の例2～9を用いた分極性電極3、4を持つ積層体10の試料2～9について行った。

【0036】E. 考察

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表3は、試料（ボタン型電気二重層コンデンサ1および積層体10を含む）1～9に関する電極密度、単位重量当りの活性炭の静電容量密度（F/g）、単位体積当りの静電容量密度（F/cc）および分極性電極の膨脹率*

* E cを示す。表3には、便宜上、表1の酸素付加物における重量増加率Yも掲載した。

【0037】

【表3】

試料	電極密度 (g/cc)	静電容量密度		分極性電極の 膨脹率 E c (%)	酸素付加物の 重量増加率 Y (%)
		(F/g)	(F/cc)		
1	0.88	35.36	31.19	70.3	1.0
2	0.80	38.17	30.38	47.0	3.5
3	0.79	38.70	29.00	38.0	5.9
4	0.80	37.56	30.00	39.5	6.7
5	0.80	38.23	30.47	40.3	9.7
6	0.84	35.88	30.00	43.0	4.3
7	0.87	35.83	31.10	42.0	5.9
8	0.85	38.06	30.62	38.0	7.4
9	0.86	36.30	31.18	37.0	10.6

【0038】図6は、試料1～9に関する酸素付加物の重量増加率Yと、分極性電極の膨脹率E cとの関係を表3に基づいてグラフ化したものである。図中、(1)～(9)は、試料1～9にそれぞれ対応する。

【0039】図6から明らかなように、酸素付加物の重量増加率Yを増加させると、分極性電極3、4の膨脹率E cが減少する。この場合、試料1の如く、酸素付加物の重量増加率YがY=1.0%では、分極性電極3、4の膨脹率E cが50%を超える。

【0040】

【発明の効果】請求項1、3記載の発明によれば、前記のような手段を採用することによって、分極性電極を構成した場合、その充電時における膨脹量を低減し得る活性炭を得ることが可能な、電気二重層コンデンサの電極用活性炭の製造方法を提供することができる。

【0041】請求項2、4、5記載の発明によれば、前記のような手段を採用することによって、分極性電極を構成した場合、その充電時における膨脹量を一層確実に低減し得る活性炭を得ることが可能な、電気二重層コンデンサの電極用活性炭の製造方法を提供することができ※

※る。

【0042】請求項6記載の発明によれば、充電時における膨脹量の小さな電気二重層コンデンサ用分極性電極を提供することができる。

【図面の簡単な説明】

【図1】ボタン型電気二重層コンデンサの要部破断正面図である。

【図2】炭素繊維の一例における酸素濃度を示すグラフである。

【図3】炭素繊維の他例における酸素濃度を示すグラフである。

【図4】炭素繊維のさらに他例における酸素濃度を示すグラフである。

【図5】分極性電極の膨脹率測定装置の概略図である。

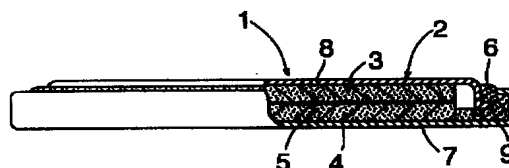
【図6】酸素付加物の重量増加率Yと、分極性電極の膨脹率E cとの関係を示すグラフである。

【符号の説明】

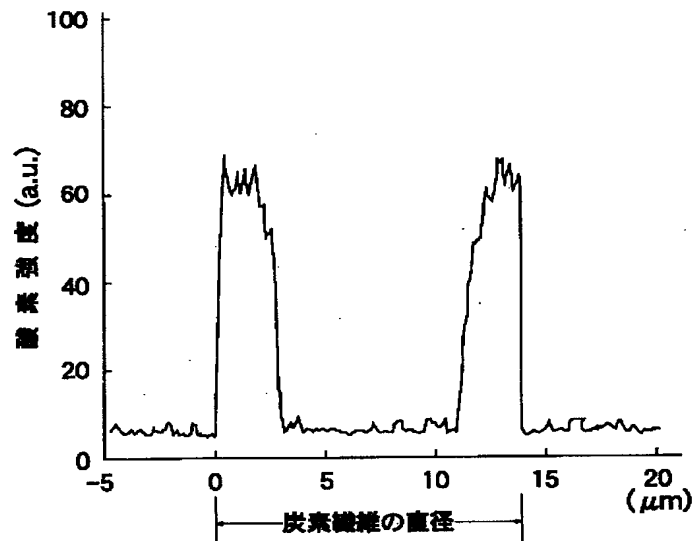
1……………ボタン型電気二重層コンデンサ

3、4……………分極性電極

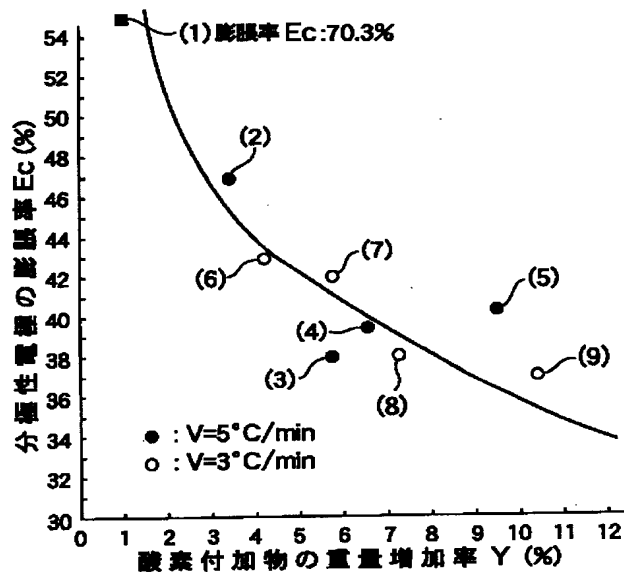
【図1】



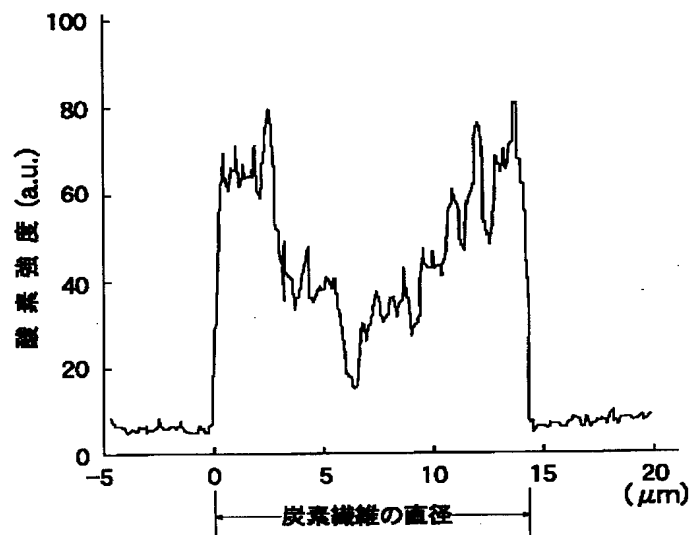
【図2】



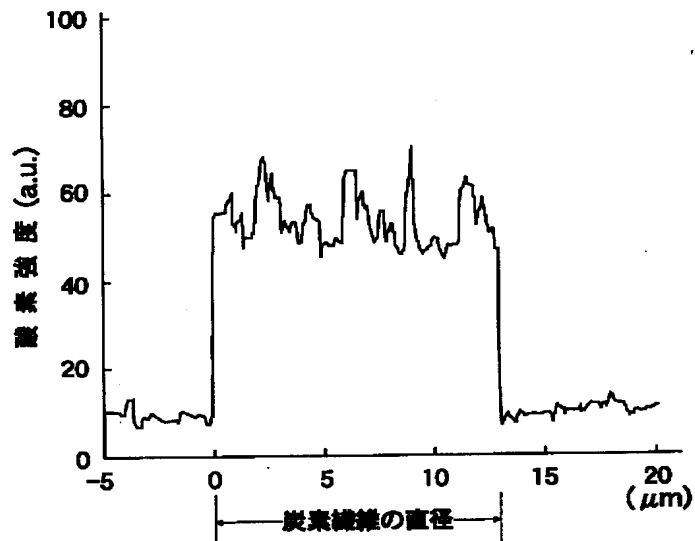
【図6】



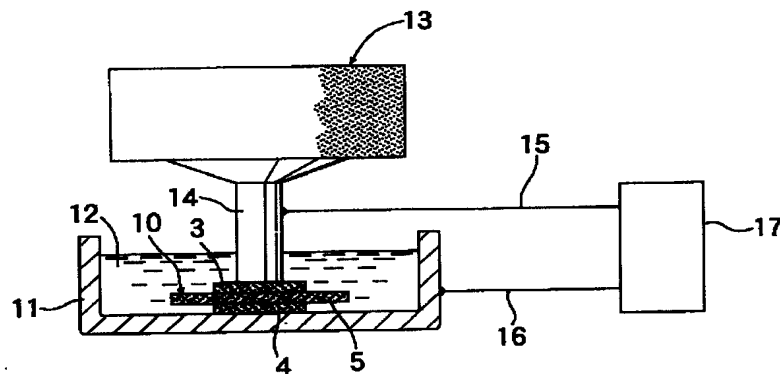
【図3】



【図4】



【図5】



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